Production of Alcohols from Olefins in Low Temperature Coal Tars

Bernard D. Blaustein, Sol J. Metlin, and Irving Wender

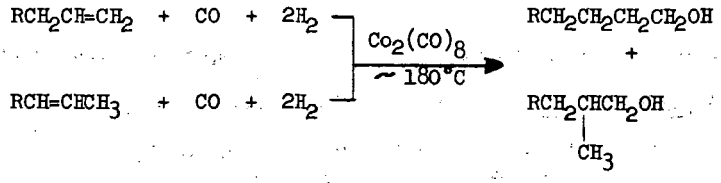
Pittsburgh Coal Research Center, Bureau of Mines
U. S. Department of the Interior
4800 Forbes Avenue, Pittsburgh 13, Pennsylvania

ABSTRACT

Olefins constitute as much as one-half the neutral oil obtained by low-temperature carbonization of low-rank coals. It is difficult to separate these olefins from other materials in the tar fractions. However, without a prior separation, a large fraction of these olefins can be converted to mixtures of primary alcohols by hydroformylation with H_2 + CO in the presence of dicobalt octacarbonyl as a catalyst (oxo reaction). Several neutral oils were so treated and the alcohols separated via their borate esters. The highest yields of alcohols (25 percent by weight of starting material) were obtained from the neutral oil of a lignite tar. The carbon number distribution of the alcohols was determined by mass-spectrometric analysis of the trimethylsilyl ethers. C_9- to C_{27}-alcohols were produced; an unusually high concentration of C_{20}-alcohols appeared in the products from lower rank coals. Nuclear magnetic resonance spectra of the alcohol mixtures showed that an "average" molecule contains from 1 to 3 branched methyl groups. By using $C^{14}O$, and assuming that each olefin will react with one CO, the percentage of olefins originally in the tar can be determined from the radioactivity of the product. An advantage of this analytical method is that no separation of the olefins, or their oxo product, need be made. By this procedure, the neutral oil from the lignite tar was shown to contain about 50 percent olefins.

INTRODUCTION

The high olefinic content of tars derived from low temperature carbonization of lower rank coals is of interest as a source of commercially valuable chemicals. However, there is no good way of separating these olefins from the other materials present in the tar fractions. The oxo (or hydroformylation) reaction offers a promising way to convert the olefins in the tar, without prior separation, to alcohols that are of potential commercial value as detergent and plasticizer intermediates. The oxo synthesis (1) is the reaction of an olefin with H_2 + CO (synthesis gas) in the presence of dicobalt octacarbonyl, $Co_2(CO)_8$, as the catalyst to yield a mixture of primary alcohols.



The reaction takes place predominantly at the terminal double bond.

The advantages of using this reaction to convert olefins to useful products are (a) the olefins need not be separated from the tar fractions to undergo reaction, (b) the reaction is not poisoned by sulfur compounds or any of the other substances in low-temperature tar, (c) conversion of the olefins is high, (d) during the oxo reaction, any internal olefinic bonds migrate to the terminal position so that all olefins react as if they were alpha olefins; all the olefins in the tar, terminal and internal, are thus utilized to make alcohols, and (e) the oxo reaction is quite versatile and can be successfully carried out under a wide range of conditions: gas pressures of 50-400 atm, and reaction temperatures of 50-200°C.; $Co_2(CO)_8$ can be used either in the preformed state, or can be formed during the reaction from a variety of cobalt salts.

EXPERIMENTAL

Samples of Rockdale lignite tar were obtained from the Texas Power and Light Company. They had separated the whole lignite tar into "methanol solubles" and "hexane solubles." The hexane solubles were further separated by distillation into two fractions, the hexane solubles foreruns (HSF) and the hexane solubles distillate (HSD). The total hexane solubles constitute 66 percent of the primary tar; the HSF 7 percent, the HSD 46 percent, and the residue from the distillation of the hexane solubles 13 percent. About 98 percent of the HSF boils below 235°C., and 89 percent of the HSD boils up to 355°C. The composition of these fractions is given in table 1.

Both fractions contain approximately 50 percent olefins, of which about half are alpha olefins (2-4). Phenolic compounds and other constituents are also present in both fractions. Since these phenols would interfere with our analytical procedure for determining alcohol yield, they were removed by chromatographing the fractions on alumina with petroleum ether as the eluting solvent. About 20 percent by weight of the starting material was removed in this way during the preparation of a "phenol-free" lignite tar fraction.

TABLE 1.-Approximate composition of low-temperature tar fractions, volume percent

Type of constituent	Hexane solubles foreruns Rockdale lignite tar	Hexane solubles distillate Rockdale lignite tar	Nugget tar distillate	Kentucky high-splint tar distillate
Caustic solubles	6-8	10-15	44	31
Acid solubles	2-4	1-3	3	7
Neutral oil	88-92	80-90	53	62
Paraffins	13-15	15-20	22	34
Olefins	40-55	40-50	20	21
Alpha-olefins	17-20	17-20		
Aromatics	30-47	35-45	37	45
Oxygenates			21	

Nugget tar, formed by the low-temperature carbonization of a hvcb-suba Wyoming coal, was also investigated. A sample of this tar was distilled under vacuum to 170°C/3mm (est. bp 320°C/760mm). The distillate, including a small amount of water phase, amounted to 42.1 percent of the whole tar. Repeated chromatography finally yielded a phenol-free neutral oil amounting to 37.9 percent of the distillate. A neutral oil derived from the low-temperature carbonization of a Kentucky hvab (high splint) coal was chromatographed on alumina to eliminate the phenols shown to be present by infrared spectral analysis. Recovery of phenol-free neutral oil was 86.8 percent.

The alcohols were separated from the oxo products by conversion to their borate esters (5-8). The borate esters formed from the alcohols are sufficiently high-boiling that the non-esterified material can be distilled away from the esters. The esters are hydrolyzed to regenerate the alcohols, which are then separated and vacuum distilled, resulting in an alcohol fraction of high purity.

$$3ROH + H_3BO_3 = (RO)_3B + 3\ H_2O$$

$$3\ ROH + (C_4H_9O)_3B = (RO)_3B + 3\ C_4H_9OH \qquad (1)$$

$$(RO)_3B + 3\ H_2O = 3\ ROH + H_3BO_3 \qquad (2)$$

In a typical run, 50 grams of chromatographed (phenol-free) HSF, 4 grams of $Co_2(CO)_8$ and 3500 psi 1:1 synthesis gas were charged into a rocking Aminco autoclave, heated to 180-190°C. and kept there for five hours. The product was treated with tri-n-butylborate (equation 1), the non-esterified material was distilled off, the borate esters were hydrolyzed

(equation 2), and the alcohols were vacuum distilled. The product was an almost water-white alcohol fraction in 25 percent yield, based on the weight of starting material. The alcohol content was confirmed by infrared spectral analysis, the only impurity detected being a small amount of a carbonyl compound. To determine the carbon number distribution of the alcohols formed, the trimethylsilyl ethers of the alcohols were analyzed by mass spectrometry (9). The results are shown in figure 1.

The chromatographed (phenol-free) HSD was subjected to the same reactions and subsequent procedures for alcohol recovery. The alcohol yield was also 25 percent by weight of the starting material; the carbon number distribution data is given in figure 2. The phenol-free neutral oil from the Nugget tar distillate was subjected to the oxo reaction and the same alcohol recovery procedures as those previously described for the Rockdale tar. An alcohol yield of 13 percent was realized. The alcohols were converted to their trimethylsilyl ethers and analyzed by mass spectrometric analysis. The results are shown in figure 3. The phenol-free neutral oil from the Kentucky hvab coal was reacted under oxo conditions. The subsequent recovery of alcohol was 7.5 percent. The product, water-white in color, was converted to trimethylsilyl ethers and submitted for mass spectrometric analysis. The results are shown in figure 4.

NMR spectra were obtained on all the alcohol mixtures produced from the tar fractions. These results will be considered in the Discussion section of this paper.

Under oxo conditions, it can be assumed that each molecule of olefin will react with one molecule of CO. Further reaction under oxo conditions will produce alcohols, aldehydes, esters, and other oxygenated products. If $C^{14}O$ is incorporated into the synthesis gas, the product will be radioactive. A determination of the amount of radioactivity in the product can then be used to calculate the concentration of olefins present originally in the tar fraction. Several runs of this type were made, both on known mixtures, and on the low-temperature tar fractions. The results obtained are discussed below.

RESULTS AND DISCUSSION

Carbon Number Distribution of Alcohols Produced

Figure 1 shows the distribution of the alcohols produced from the HSF fraction of the lignite tar. The carbon number range shown is C_{10}-C_{15}, the maximum concentration is at C_{12}, and the average carbon number is 12.2. Not shown on the graph are minor concentrations of C_9 and C_{16}-C_{20} alcohols. This mixture is composed of alcohols of the carbon number

range now used for plasticizer and detergent production. A higher boiling fraction of these alcohols ranged from C_9 to C_{24}, with an average carbon number of 16.2. Figure 2 shows the distribution of the alcohols produced from the HSD fraction of the lignite tar. The carbon number range shown is C_{13}-C_{22}, the largest percentage is at C_{20}, and the average carbon number is 17.8. There are also traces of C_{11}-C_{12} and C_{23}-C_{27} alcohols.

Figure 3 shows the distribution of alcohols produced from the neutral oil from the Negget tar distillate. The carbon numbers range from C_{11}-C_{23}, the largest concentration is at C_{15}, and the average carbon number is 16.3. Trace amounts, not shown, are also present at C_{24} and C_{25}. Figure 4 shows the distribution of the higher boiling alcohols produced from the neutral oil from the Kentucky hvab coal. The carbon numbers range from C_{13}-C_{23}, the greatest concentrations are at C_{16} and C_{17}, and the average carbon number is 17.2. Trace amounts, not shown, were also present at C_{24}. A lower boiling fraction of these alcohols ranged from C_{10} to C_{22}, with an average carbon number of 14.1.

In the alcohol mixtures produced from the lower rank lignite and hvcb-suba coals, there are anomalously high concentrations of C_{20} alcohols. (See figures 2 and 3.) This did not appear in the alcohols from the hvab coal (figure 4). Gas-chromatographic methods, and other separation techniques, will be used to obtain highly concentrated samples of either the C_{20} alcohols and/or their precursors, the C_{19} olefins from the lignite tar. If identification of either the alcohols or olefins can be made, it may point out interesting differences between the low-temperature carbonization tars produced from low and medium rank coals. It is conceivable that the C_{19} olefin present in such high concentration in the tars from the lower rank coals is some isomer of pristene (2,6,10,14-tetramethylpentadecene), since the saturated paraffin, pristane, recently has been isolated from a low-temperature brown coal tar (10), and was shown to be present in abnormally high concentrations in two petroleums (11).

NMR Spectra of Alcohol Mixtures

The NMR spectra of these alcohol mixtures were run on a Varian HR-60 instrument. Data were obtained for the number of H atoms on the C atom bonded to the OH group (that is, if the alcohol is a primary alcohol), and the number of H atoms present in methyl groups. This latter quantity gives a measure of the branching of the carbon chain.

For the HSF alcohols, there were 1.8 H atoms on C bonded to OH, and 1.8 methyl groups/molecule; HSD, 1.9 H, 3.4 methyl; Nugget, 2.3 H, 3.0 methyl; and Kentucky, 1.9 H, 2.6 methyl. Within the accuracy of the method, all

of the alcohols appear to be primary, as expected from the nature of the oxo reaction. In general, the number of branched methyl groups increases with the average carbon number of the alcohol mixture. As a comparison with some other, more highly branched, commercially-produced oxo alcohols, C_{13}-alcohols made from triisobutylene would have at least 6 methyl groups/molecule; those made from tetrapropylene would have at least 4 methyl groups/molecule; and C_{17}-alcohols made from tetraisobutylene would have at least 8 methyl groups/molecule.

Determination of Olefin Content of Mixtures by Using $C^{14}O$

If a mixture containing olefins is reacted with H_2 + $C^{14}O$, to a good approximation, each molecule of olefin will react with one molecule of CO, and therefore each olefin will be "tagged" with radioactivity. This will be true whether the olefin ends up as an alcohol, aldehyde, ester, ether, etc. The only exception is when the olefin hydrogenates to form the paraffin, and this is an important reaction under oxo conditions only for highly branched olefins, or compounds such as indene.

By measuring the radioactivity of the total oxo product obtained from each olefin-containing fraction relative to the radioactivity of the residual CO in equilibrium with the bomb contents at the end of the run, the initial olefin content of the mixture can be determined. In each 100 molecules of the olefin-containing mixture, where x molecules are olefinic, and Y is the average carbon number of the mixture;

$$\frac{x}{100\ Y + x}\ \text{(radioactivity of gas in bomb at end of run)} = \text{(radioactivity of product)}.$$

Table 2 gives the results obtained by this procedure. Agreement between

TABLE 2.-Determination of olefin content of mixtures by using $C^{14}O$

Mixture	Assumed average carbon number	Olefin Content, mole percent Known	Found
Decene-1 + 1-methylnaphthalene	10.0	47 50	52 56
Decene-1 + dodecene-1 + limonene + 4-methylcyclohexene-1 + 1-methylnaphthalene	9.5	55	53
HSF	12.4	1/ 40-55	55, 48
HSD	16.8	1/ 40-50	53, 42

1/ See table 1.

known and found values is satisfactory. Further work is being done on the other tar fractions, and on improving the accuracy of this analytical procedure.

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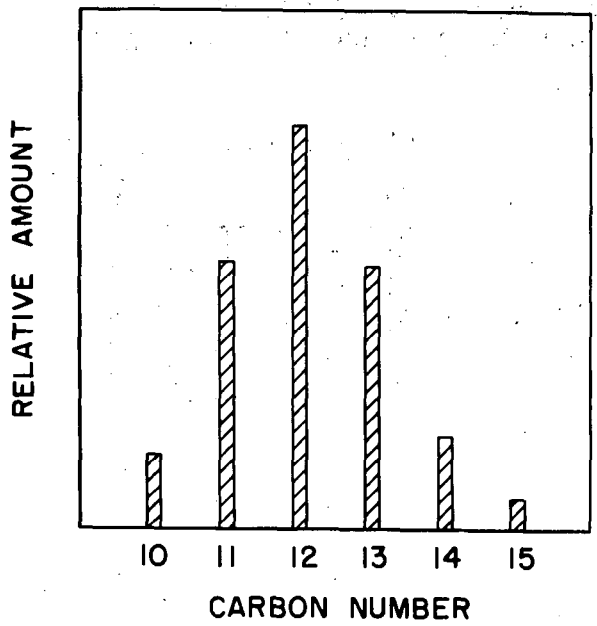

Figure 1.- Distribution of alcohols produced from hexane solubles foreruns fraction of Rockdale lignite tar.

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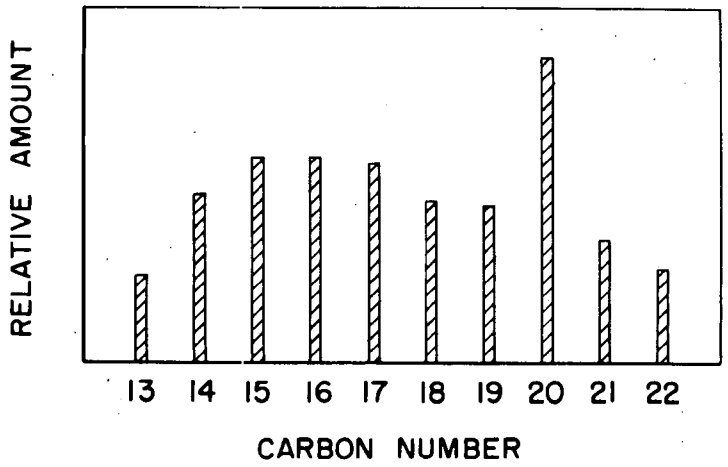

Figure 2.-Distribution of alcohols produced from hexane solubles distillate fraction of Rockdale lignite tar.

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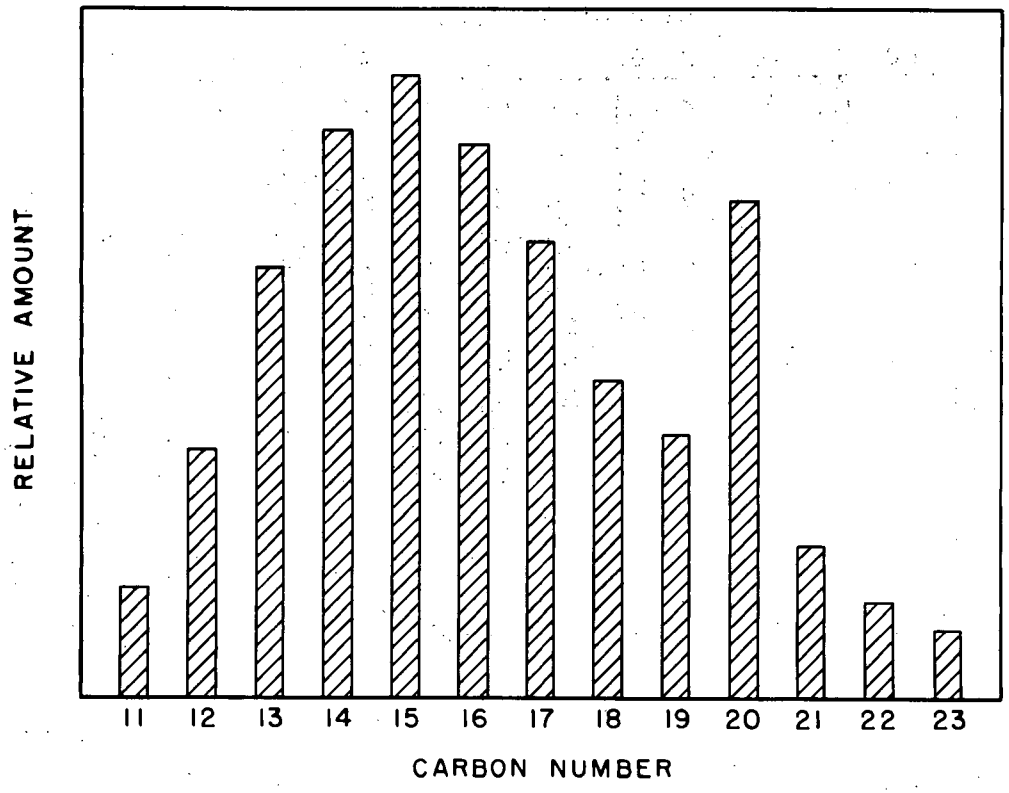

Figure 3. — Distribution of alcohols from nugget tar neutral oil produced from a Wyoming hvcb-suba coal.

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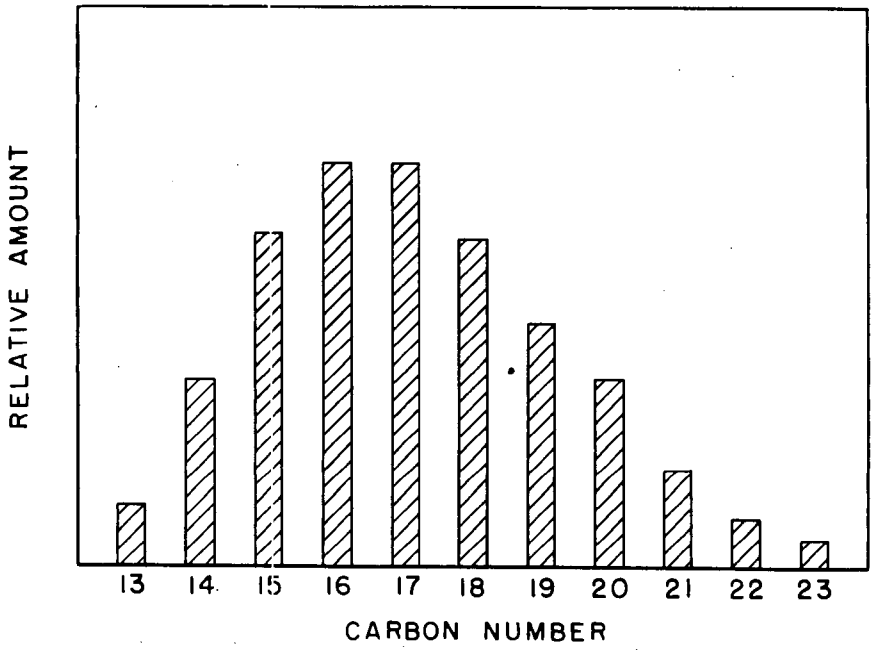

Figure 4.- Distribution of alcohols from a low-temperature tar neutral oil produced from a Kentucky hvab (high splint) coal.